Photocatalytic treatment under visible light applied to aqueous glyphosate solution

Tratamento fotocatalítico sob luz visível aplicado à solução aquosa de glifosato

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Numerous chemical residues produced by industries and agricultural activities harm the environment. Pesticides and herbicides pollute soil and water and have toxic effects on living beings. Glyphosate – N-(phosphonomethyl)glycine – is an herbicide extensively used for the non-selective control of weeds. This systemic and post-emergent organophosphorus compound accounts for 60% of the world market of non-selective herbicides. Photocatalysis is one of the safest and least expensive methods for removing pesticides from wastewater. Evidence in the literature shows that photocatalysis has the potential for the removal of herbicides from surface waters and soil. The present study aimed to investigate the photocatalytic degradation and reduction of phytotoxicity of glyphosate in the presence of cerium dioxide (CeO_2), titanium dioxide (TiO_2) and zinc oxide (ZnO) as catalysts (2 g L^{-1}) under a visible radiation source. Among the catalysts, CeO_2 had the best efficiency, achieving 17% degradation, followed by ZnO (6.8%) and TiO_2 (6.4%). The concentration of CeO_2 was diminished to 1 g L^{-1} to assess its influence, leading to a reduction in degradation from 17% to 15%. Phytotoxicity of the product of the reactions was also evaluated and revealed a nonphytotoxic compound was formed in the photocatalytic reaction solution using CeO_2 as the catalyst.
Keywords: photocatalysis, herbicide, water treatment.

Muitos resíduos químicos produzidos pela indústria e por atividades agrícolas são prejudiciais ao meio ambiente. Pesticidas e herbicidas causam poluição no solo e nas águas, além de poder apresentar efeitos tóxicos para os seres vivos. O glifosato, N-(fosfometil)glicina, é um herbicida amplamente utilizado no controle não seletivo de ervas daninhas. O composto organofosforado, sistêmico e pós-emergente, representa 60% do mercado mundial de herbicidas não seletivos. Um dos métodos para a remoção de pesticidas de águas residuais mais seguro e menos dispendioso é a fotocatálise. Evidências na literatura mostram que a fotocatálise apresenta potencial para a remoção de contaminantes herbicidas presentes em águas superficiais e no solo. Neste trabalho foi avaliada a degradação fotocatalítica e redução de fitotoxicidade de glifosato na presença de dióxido de cério (CeO_2), dióxido de titânio (TiO_2) e óxido de zinco (ZnO) como catalisadores (2 g L^{-1}) sob fonte de radiação visível. Dentre os catalisadores empregados, o CeO_2 obteve a maior eficiência com 17% de degradação, seguido do ZnO com 6,8% e TiO_2 com 6,4%. A concentração de fotocatalisador CeO_2 foi diminuída para 1 g L^{-1} para analisar sua influência e observou-se redução na degradação de 17% para 15%. Foi avaliada também a fitotoxicidade do produto das reações, sendo constatada a formação de composto não fitotóxico na reação de fotocatálise utilizando CeO_2 como catalisador.
Palavras-chave: fotocatálise, herbicida, tratamento de água.

1. INTRODUCTION

Glyphosate – N-(phosphonomethyl)glycine – is a non-selective broad-spectrum herbicide and the active ingredient in the brand names Roundup® and Rodeo® produced by Bayer, often used to control weeds and grasses [1]. The post-emergent, systemic, non-selective organophosphorus

compound accounts for most of the world market of non-selective herbicides and approximately 60% of herbicide applications in Brazil [2].

The Monsanto Company announced that glyphosate is highly safe, justifying this by its main toxicity mechanism that affects a metabolic pathway in plant cells that human cells do not possess. Theoretically, this mechanism makes glyphosate effective at killing plants while leaving humans and other animals unharmed. However, the pathway by which glyphosate affects plants is found in nearly all intestinal microorganisms in human beings [1]. The International Agency for Research on Cancer (IARC) analyzed 36 active ingredients of pesticides and herbicides, 15 authorized for use in Brazil, with diazinon, glyphosate, and malathion classified as probable carcinogens [3].

Photocatalytic degradation is a promising method for treating wastewater contaminated with organic and inorganic compounds. As pollutants can be degraded entirely using room temperature and atmospheric pressure methods, photocatalysis is considered one of the most productive ways to deal with different types of wastewater [4, 5]. Compared to traditional treatment methods, photocatalysis is an efficient, ecological method for converting contamination targets into small, non-toxic molecules through electromagnetic radiation emission [6, 7]. This method can also be defined as the acceleration of a photoreaction through the action of a catalyst. Photocatalysis is a very simple process. Photons activate the semiconductor photocatalyst, establishing an oxidation reaction in an aqueous solution. A semiconductor serves as a sensitizer for the redox process induced by light due to its electronic structure, characterized by a full valence band and an empty conduction band. The difference in energy between the valence and conduction bands is called the band gap [8].

Some metal oxides stand out among the various semiconductors due to their potential as photocatalysts. Titanium dioxide (TiO_2) is considered one of the most adequate for general environmental applications due to its biological and chemical inertia, low cost and long-term stability against photo-corrosion and chemical corrosion. Chen and Liu (2007) [4] used TiO_2 as a photocatalyst for the removal of glyphosate. With a load of 6.0 g L^{-1}, the authors reported the ease with which the oxide degraded the herbicide under ultraviolet (UV) irradiation (mercury lamp with an average pressure of 375 W), degrading 50.2% of the molecules of the pollutant in a solution in one hour of irradiation [4].

Khan and Pathak (2020) [8] conducted studies using zinc oxide (ZnO) as the photocatalyst. The authors state that this oxide is less aggressive to the environment due to its compatibility with living organisms. Thus, the compound has received considerable attention in remedying environmental problems caused by pollutants. This oxide has high photoactivity in the UV direction and near the visible range, inertia, low cost, low environmental toxicity, and resistance to photo-corrosion. ZnO has a band gap similar to that of TiO_2, which suggests similar photocatalytic efficiency.

Cerium dioxide (CeO_2) has been increasingly applied in photocatalysis due to its strong absorption of UV radiation, good oxygen transport capacity, unique Ce^{4+}/Ce^{3+} redox cycle, and good biocompatibility. CeO_2 has a band gap of 2.94 eV, enabling photonic activation at less energetic wavelengths near the visible region of the spectrum, which generates lower energy expenditure, enabling the use of solar radiation. Using reactors without the need for UV lamps facilitates its application in the heterogeneous photocatalytic process for the degradation of pollutant compounds [9]. Wu et al. (2021) [6] investigated the catalytic photodegradation of glyphosate using nanoparticles of CeO_2 as the dispersed catalyst at an ideal concentration of 0.25 g L^{-1}. Significant catalytic activity was found under visible light, dependent on the size of the catalyst nanoparticle. The authors also concluded that the direct photolysis of glyphosate is limited in visible light (800 W m^{-2} and 1800 W m^{-2}), but the catalyst molecules have noteworthy adoption capacity and catalytic activity.

Some glyphosate degradation products can be more toxic and persistent than glyphosate itself. The potential toxicity and common occurrence of glyphosate highlight the importance and urgency in understanding the fate and persistence of this organophosphate compound and its degradation products in soil and other environments [10].

During the degradation of glyphosate, the cleavage of four bonds is involved in determining intermediaries. Besides the formation of aminomethylphosphonic acid (AMPA) by the

breakdown of the C-C bond or C-N bond on the side similar to glycine (AMPA pathway), another path involves the cleavage of a C-P or C-N bond at the phosphonomethyl extremity, which would lead to the production of sarcosine or glycine (sarcosine pathway). The preferential cleavage of the C-N bond adjacent to phosphonate is obtained to form comparatively benign glycine or for the release of orthophosphate, which has scientific and environmental importance in less toxic glyphosate degradation pathways. The AMPA pathway is considered the dominant degradation mechanism of glyphosate while sarcosine pathway is more uncommon [11-13].

The assessment of the phytotoxicity of a compound is critical, as it enables determining the existence of substances that can inhibit seed germination, root growth, or plant development. The phototoxic quantification of a given compound is commonly used as a maturation indicator of the compound. Among the methods found in the literature, tests with plants are the most widely employed and offer numerous advantages, enabling the simultaneous assessment of the effects caused by phytotoxic factors. However, such tests do not identify the specific contaminants that cause toxicity [14].

The present study aimed to compare the removal of the herbicide glyphosate by photocatalysis using titanium dioxide (TiO_2), cerium dioxide (CeO_2) and zinc oxide (ZnO) as dispersed photocatalysts under radiation in the visible range and assess the phytotoxicity of the product of the reactions, investigating the effect of different concentrations of the catalyst.

2. MATERIALS AND METHODS

2.1 Preparation of solutions

A volume of 500 mL solution with a glyphosate concentration of 50 mg L^{-1} was prepared before each reaction. Fifty 50 mL of 5% ninhydrin solution (NEON – 99% purity) and 50 mL of 5% sodium molybdate solution (ÊXODO CIENTÍFICA – 99.5% purity) were prepared. Both solutions were placed in amber flasks and stored in a dark dry place.

2.2 Reaction

To compare photocatalytic degradation efficiency among the catalysts, experiments were conducted using the same initial concentration of the herbicide (50 mg L^{-1}) together with the same load of the catalyst (2 g L^{-1}). The previously prepared glyphosate solution was added to a 600 mL batch reactor and placed in an isolation chamber. Photolysis with irradiation alone was performed before the reactions in the presence of the photocatalysts. For the reactions in the presence of the photocatalysts, TiO_2 (NEON 98%), CeO_2 (ÊXODO 99%) and ZnO (DINÂMICA 99%) were added to the reactor at a load of 2 g L^{-1} for each reaction. Subsequently, a CeO_2 load of 1 g L^{-1} was used. Each catalyst was assessed individually in the reaction.

The reactor was positioned over a magnetic stirrer approximately 35 cm below a mercury vapor lamp (G-light - 400W). The system was isolated by a metal box with a front opening and two lateral coolers for internal air circulation. The system also had a digital temperature indicator (Figure 1).
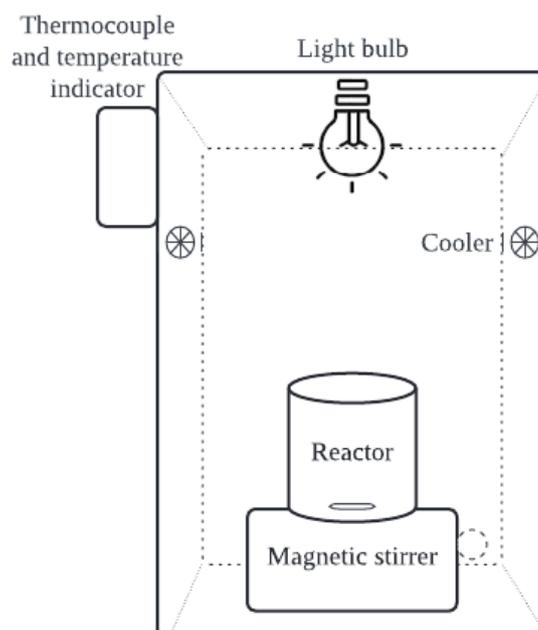
Figure 1: Illustration of reactional apparatus used in photodegradation experiments.

Reaction time was 2 h and 30 min. In the presence of the photocatalysts, the reaction remained under agitation in the dark for 30 min to reach the adsorption-desorption equilibrium. All reactions were performed in duplicate.

Samples (5 mL) were withdrawn every 30 min during the reaction. The samples were filtered using a syringe filter with 45-µm pores to remove possible catalyst particles and halt the reaction. Each sample was stored in a dark tube and analyzed using a benchtop spectrophotometer (KASVI: k37 UVVIS).

2.3 Derivatization and spectrophotometric reading

A method adapted from Bhaskara and Nagaraja (2006) [15] was used for the spectrophotometric quantification of glyphosate. This method is based on the derivatization of glyphosate, as the compound's chemical structure does not have a chromophore group. The method consists of adding 1 mL of the sample containing glyphosate, 1 mL of the 5% sodium molybdate, and 1 mL of the 5% ninhydrin solution to a test tube, which is heated in a water bath at 100 ℃ for 10 min, as shown in Figure 2.

In this reaction, ninhydrin is the chromophore agent, and sodium molybdate is the catalyst. After derivatization, the solution has a purplish color with maximum absorbance at 570 nm. The sample was then cooled to room temperature, and the reading was performed in a benchtop spectrophotometer. This process was conducted in triplicate.

Mean absorbance was calculated from the three spectrophotometric readings of each sample reaction, followed by the calculation of the percentage of degradation using Equation 1, in which A is absorbance measured during the reaction time, and A_0 is the absorbance of the sample collected immediately before exposure of the medium to visible radiation.

$$Degradation(\%) = (1 - \frac{A}{A_0}) \times 100 \qquad (1)$$

This method is simple, fast and does not require extraction procedures. With this method, ninhydrin reacts with primary and secondary amines in the solution. Thus, it is impossible to distinguish glyphosate from aminomethylphosphonic acid and other degradation products [15].
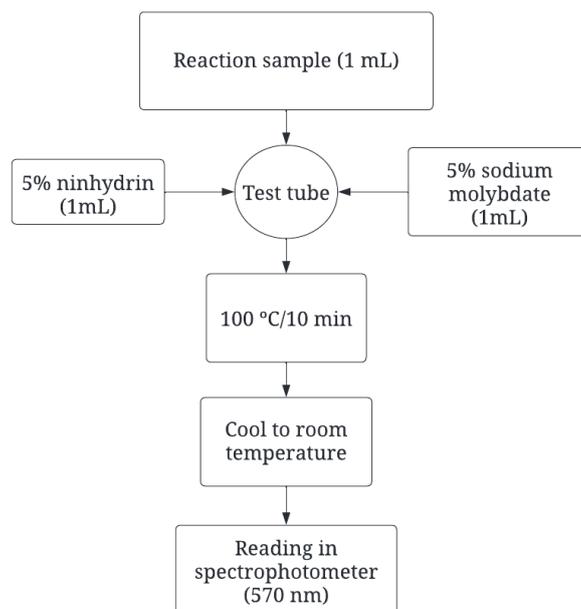
Figure 2: Block diagram of glyphosate derivatization procedure.

2.4 Toxicity

The filter paper was placed in a previously autoclaved Petri dish and moistened with 5 mL of solution. For the tests, an initial solution of glyphosate (50 mg L^{-1}) was used after the photolysis reaction with each catalyst: ZnO, TiO$_2$ and CeO$_2$ (2 g L^{-1} and 1 g L^{-1}). Another dish was prepared with distilled water as the control. Twenty seeds of *Lectuca sativa* were evenly distributed in each dish. The assays remained for 120 h (5 days) in the dishes, which were sealed with plastic (PVC) wrap and placed in the BOD incubator (7Lab - BioBod120) at 22ºC. The procedure was performed in duplicate. After 120 h, the average number of seeds that germinated ($\overline{GS}$) and the average length of the roots ($\overline{RL}$) in each dish was recorded. These variables enabled the calculation of the germination index (*GI*) using Equation 2.

$$GI(\%) = \frac{\overline{RL}sample \times \overline{GS}sample}{\overline{RL}control \times \overline{GS}control} \times 100$$

(2)

The quantitative classification of the phytotoxicity of the samples to L. sativa followed the method described by Pinho et al. (2017) [14], in which a *GI* more significant than 100% denotes a solution that enables germination and root growth, 80% to 100% constitutes a nonphytotoxic matured compound, 60% to 80% corresponds to a moderately phytotoxic solution, 30% to 60% corresponds to a phytotoxic solution and less than 30% denotes a very phytotoxic solution.

3. RESULTS AND DISCUSSION

Treatment only with visible light (without the presence of the photocatalysts) was performed to assess the effect of direct photolysis on the reactions. The variation around zero revealed that this treatment achieved negligible results for the conditions analyzed. Thus, one may state that glyphosate is stable in the presence of radiation in the visible range under the conditions tested in the present study.

Figure 3 shows the percentage of glyphosate degradation by heterogeneous photocatalysis as a function of visible light irradiation time. Degradation was more significant when the cerium dioxide (CeO$_2$) catalyst was used compared to that achieved in the presence of zinc oxide (ZnO)

and titanium dioxide (TiO$_2$). After 90 min of irradiation, degradation presented stability; CeO$_2$ achieved 17% degradation, whereas ZnO and TiO$_2$ achieved 6.8% and 6.4%, respectively.
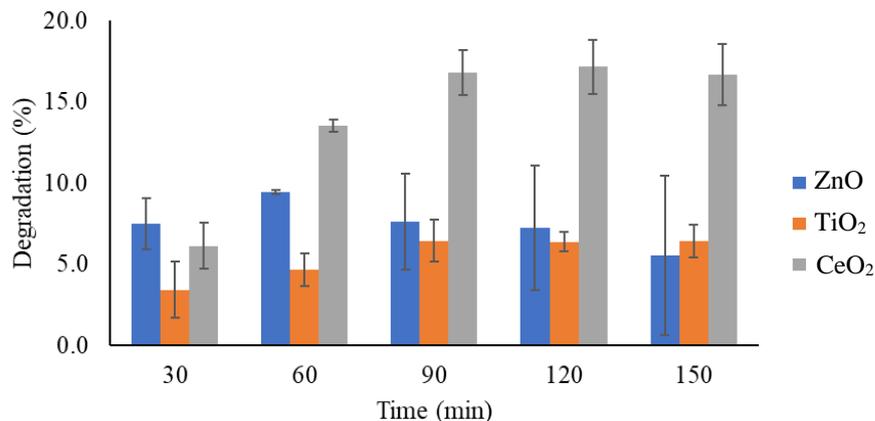

Figure 3: Degradation kinetics of glyphosate with 2 g L^{-1} of ZnO, TiO$_2$ and CeO$_2$ photocatalysts under visible light radiation.

Kesarla et al. (2019) [16] synthesized CeO$_2$ nanoparticles from CeCl$_3$ with the aid of l-arginine and anchored the nanoparticles to nanosheets of gC$_3$N$_4$. Photocatalytic activity was assessed using an air-cooled 1500 W exon light. During the experimental run, 30 mg of the photocatalyst was dispersed in 200 mL of a solution with the herbicide Diuron at a concentration of 25 mg L^{-1} and kept in the dark for 60 min under stirring to establish the adsorption-desorption equilibrium. During 120 h of irradiation in the presence of the photocatalyst, the concentration of Diuron was reduced by 15.34% and 46% with gC$_3$N$_4$ and the gC$_3$N$_4$/CeO$_2$ composite, respectively. The authors concluded that nitrogen doping in CeO$_2$ reduced the band gap of the composite, which explains its better photodegradation performance.

Tang et al. (2021) [17] assessed nanoparticles of CoS deposited on the surface of 2D BiOBr nanosheets to fabricate novel ultrathin photocatalysts in close contact. Under visible light irradiation (44 W LED lamp), the apparent reaction rate constant of the degradation of glyphosate reached 74.7% in 3 h. The authors attributed the photocatalytic performance to the strong absorption of visible light, effective charge separation, and low resistance to the charge transfer of the photocatalyst.

Figure 4 shows the slight variation in the glyphosate removal rate when the photocatalyst load is diminished. For the initial load of 2 g L^{-1}, degradation was 17% after 90 min of irradiation, whereas degradation was 15% after 90 minutes of degradation when the initial photocatalyst load was 1 g L^{-1}. Wu et al. (2021) [6] assessed the effect of the concentration of CeO$_2$ on degradation efficiency and found a reduction in degradation with the decrease in the catalyst load.
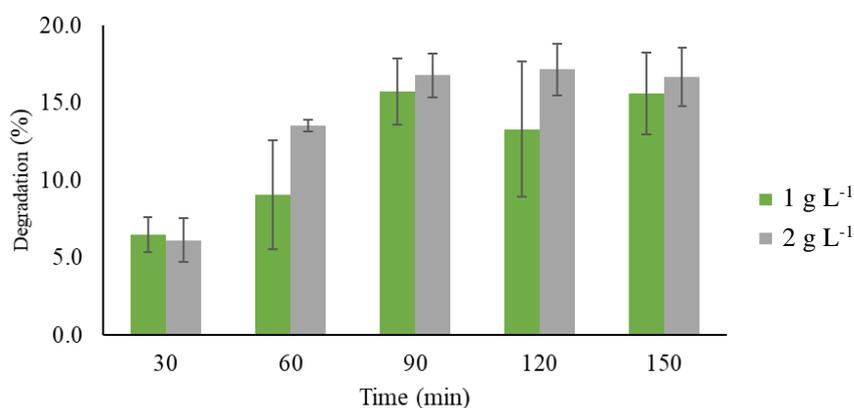

Figure 4: Effect of concentration of CeO$_2$ photocatalyst on glyphosate degradation kinetics.

In the study conducted by Li et al. (2016) [10], the degradation kinetics of glyphosate by heterogeneous photocatalysis revealed that the glyphosate degradation rate was greater than that of AMPA under all experimental conditions. Huang et al. (2021) [11] also found a predominance of AMPA pathways compared to the sarcosine pathway during the photocatalytic degradation of glyphosate. The formation of this byproduct during the herbicide degradation suggests that the actual degradation of glyphosate in the experiments conducted in the present study may be more significant, as it was not possible to distinguish both compounds by the derivatization method employed. With this method, the chromophore agent reacts with primary and secondary amines in the solution, and it is impossible to distinguish glyphosate from aminomethylphosphonic acid and other degradation products.

A complementary way to assess the efficiency of photocatalytic treatment is through the analysis of phytotoxicity. After 2 h and 30 min reactions, phytotoxicity was evaluated as described in the methods section. None of the samples in any treatment had a germination index as high as 31.1%, indicating phytotoxic behavior. The samples submitted to photocatalytic degradation with ZnO and TiO_2 and the sample submitted to photolysis alone also exhibited phytotoxic behavior, with germination indices (GI) of 35.9%, 50.9% and 56.1%, respectively, indicating that toxicity was not altered due to treatment.

However, a reduction in toxicity was found in the samples for which the photocatalytic process was performed in CeO_2. The germination index was 77.4% when 1 g L^{-1} of the photocatalyst was used, indicating moderate phytotoxicity, and 83.3% when the load was 2 g L^{-1}, indicating that this effluent can be classified as non-toxic or a matured compound, according to Pinho et al. (2017) [14].

Regarding the phytotoxic result of degradation by TiO_2, a slight reduction was found in comparison to the initial solution, suggesting the non-real detection of degradation, as the photocatalyst did not exhibit much efficiency in terms of degradation. Even with relatively low degradation in the presence of CeO_2, the solutions achieved a satisfactory result regarding phytotoxicity. In the reaction with the CeO_2 photocatalyst, the mean absorbance after 30 min in the dark was slightly lower than the reactions using the other photocatalysts. According to Wu et al. (2021) [6], particles of the CeO_2 photocatalyst have considerable adsorption capacity, which suggests the contribution of this effect to the reduction in the final phytotoxicity of the reaction. However, it should be pointed out that the initial content considered in the estimate of the degradation rate was measured after the adsorption equilibrium period.

For the reaction with 2 g L^{-1} of the CeO_2 photocatalyst, the solution exhibited a nonphytotoxic nature (matured compound), suggesting possible high herbicide degradation but not entirely detected by the derivatization method employed. The fact that the solution was nonphytotoxic also suggests the strong influence of possible adsorption of the N-phosphonomethylglycine molecules to the photocatalyst molecule. When the load of the catalyst was diminished, a certain degree of phytotoxicity was found, but much lower than that of the initial solution.

The assessment of the photocatalytic degradation of glyphosate in the presence of the dispersed CeO_2 photocatalyst under visible light and the assessment of phytotoxicity to *L. sativa* seeds revealed the relevant removal of phytotoxic compounds present in the solution, considering a matured compound as the result of the test for this reaction. Apparent degradation was 17%, and this photocatalyst was more efficient than TiO_2 and ZnO under the same reaction conditions.

4. CONCLUSION

The photocatalytic degradation of glyphosate under visible light was executed simply and directly. The degradation rate was 17% with the CeO_2 catalyst, 6.8% with ZnO and 6.4% with TiO_2. Despite the relatively low apparent degradation rate, the results achieved with CeO_2 are satisfactory when analyzed in conjunction with phytotoxicity. This offers strong indications that the derivatization method has low selectivity in relation to the glyphosate molecule and that the real degradation of the herbicide may be higher than that presented herein. The results demonstrate that heterogeneous photocatalysis in a batch reactor under environmental conditions

and visible light irradiation is a promising method for removing the herbicide and consequent reduction in the phytotoxicity of agricultural organophosphorus residues.

5. ACKNOWLEDGMENTS

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